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BP CHEMICALS LIMITED
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Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

UNITED KINGDOM

4141891002

4. Title of the invention

AUTOTHERMAL CRACKING PROCESS

5. Name of your agent (if you have one)

HAWKINS, David George

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

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11. I/We request the grant of a patent on the basis of this application.

Signature  Date 18.12.03

HAWKINS, David George

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AUTOTHERMAL CRACKING PROCESS

The present invention relates to the production of mono-olefins by autothermal cracking of a paraffinic hydrocarbon having two or more carbon atoms especially autothermal cracking of ethane, propane, and butanes.

Olefins such as ethene and propene may be produced by a variety of processes including the steam cracking of hydrocarbons or by the dehydrogenation of paraffinic feedstocks. More recently olefins have been produced by a process known as autothermal cracking. In such a process a paraffinic hydrocarbon feed is mixed with an oxygen-containing gas and contacted with a catalyst which is capable of supporting combustion beyond the normal fuel rich limit of flammability to provide a hydrocarbon product stream comprising olefins. The hydrocarbon feed is partially combusted and the heat produced is used to drive the dehydrogenation reaction. Such a process is described in EP-B1-0332289.

The steam cracking of hydrocarbons to produce mono-olefins normally co-produces other unsaturated hydrocarbons e.g. dienes and alkynes.

The dienes are usually separated from the steam cracker product stream which involves the use of large amounts of toxic flammable solvents e.g. acetonitrile. Once separated the dienes are considered high value products and are used in derivative processes e.g. elastomer production. However dienes are difficult to transport because they are readily degraded via oligimerisation and consequently derivative plants that employ diene feedstock are usually co-located with the sources of supply. Where there is no derivative capacity to use the dienes the production of dienes becomes problematic. This is because it is not desirable that dienes be recycled to a steam cracker due to their high propensity to cause carbonaceous fouling of the

process equipment and therefore the dienes must be hydrogenated before being recycled to the steam cracker, or short furnace run-times must be tolerated, with consequent financial and operational disadvantages.

Similar problems arise with other unsaturated hydrocarbons produced by steam cracking, such as alkynes and aromatics. These also have a high propensity to cause carbonaceous fouling if recycled to a steam cracker, and therefore must be hydrogenated before recycling, or short furnace run-times must be tolerated.

It has now been found that the autothermal cracking process can tolerate co-feeding unsaturated hydrocarbons without carbonaceous fouling. More particularly, it has now been found that the autothermal cracking process can be improved by co-feeding at least one unsaturated hydrocarbon, in particular a diene or alkyne, with the paraffinic hydrocarbon feed and the molecular oxygen-containing gas to the autothermal cracker. It has been found that co-feeding at least one unsaturated hydrocarbon provides an increase in the olefin yield based on the amount of paraffinic hydrocarbon feed converted. Without wishing to be bound by theory, this is believed to be due to the propensity of co-fed unsaturated hydrocarbons to combust in preference to paraffinic hydrocarbons in the feed. Furthermore it has been found that the majority of the unsaturated hydrocarbon can be converted and, surprisingly, no significant carbon formation occurs on the catalyst, and unexpectedly low amounts of additional compounds e.g. benzene or toluene, associated with carbon formation on the catalyst are produced.

Accordingly, the present invention provides a process for the production of olefins which process comprises feeding a paraffinic hydrocarbon, at least one unsaturated hydrocarbon and a molecular oxygen-containing gas to an autothermal cracker wherein they are reacted in the presence of a catalyst capable of supporting combustion beyond the normal fuel rich limit of flammability to provide a hydrocarbon product stream comprising olefins.

The paraffinic hydrocarbon and the at least one unsaturated hydrocarbon may both be provided as a single hydrocarbon-containing feedstock. Suitably, the hydrocarbon-containing feedstock comprises at least 5wt%, such as 5 to 50wt% of unsaturated hydrocarbons based on the weight of paraffinic hydrocarbons.

Alternatively, the paraffinic hydrocarbon is provided as a paraffinic hydrocarbon-containing feedstock (which may also contain unsaturated hydrocarbons),

and at least one unsaturated hydrocarbon is provided as a separate stream to that of the paraffinic hydrocarbon-containing feedstock.

Accordingly the present invention provides a process for the production of olefins which process comprises feeding a paraffinic hydrocarbon-containing feedstock, at least one unsaturated hydrocarbon and a molecular oxygen-containing gas to an autothermal cracker wherein they are reacted in the presence of a catalyst capable of supporting combustion beyond the normal fuel rich limit of flammability to provide a hydrocarbon product stream comprising olefins.

A single unsaturated hydrocarbon or a mixture of unsaturated hydrocarbons may be passed to the autothermal cracker.

"Unsaturated hydrocarbon", as used herein, includes olefins.

Thus, the unsaturated hydrocarbon may be an alkene such as ethene, propene, butenes, pentenes, hexenes, heptenes, higher alkenes and cycloalkenes, such as cyclopropene, cyclobutene, cyclopentene(s), cyclohexene(s), cycloheptenes and higher cycloalkenes.

The unsaturated hydrocarbon may be an aromatic compound. Any aromatic compound may be used, e.g. benzene, toluene, xylenes, ethylbenzene, styrene and substituted styrenes, indene and substituted indenenes. Preferably, the aromatic compound may be benzene or toluene.

In a first preferred embodiment the unsaturated hydrocarbon is a diene. The diene(s) may be selected from any suitable dienes but are preferably selected from propadiene, 1,2 butadiene, 1,3 butadiene, 1,3 pentadiene, 1,4 pentadiene, cyclopentadiene, 1,3 hexadiene, 1,4 hexadiene, 1,5 hexadiene, 2,4 hexadiene, 1,3 cyclohexadiene and 1,4 cyclohexadiene, and substituted derivatives of the above, e.g. alkyl substituted derivatives, eg methyl derivatives with more than one substitution per molecule, wherein the substituents may be the same or different. Most preferably the diene(s) are selected from 1,2 butadiene, 1,3 butadiene, 2 methyl 1,3 butadiene, 1,3 pentadiene, 1,4 pentadiene and cyclopentadiene. Advantageously the diene is 1,3 butadiene.

In a second preferred embodiment, the unsaturated hydrocarbon may be an alkyne such as acetylene, propyne and/or a butyne. A particularly preferred alkyne is acetylene.

The process for the production of olefins according to the present invention

produces predominantly mono-olefins (alkenes), especially ethene and propene, although quantities of other olefins may also be produced.

Although alkenes may be co-fed without carbonaceous fouling of the process, and may be expected to combust in preference to paraffinic hydrocarbons in the feed, it is generally preferred not to co-feed alkenes which are the same as the desired products of the process. However, co-feed of alkenes which are the same as the desired products of the process may take place if they are present as part of a stream also comprising other unsaturated hydrocarbons. Alternatively, for example, although it is generally preferred not to co-feed ethene and/or propene to an autothermal cracker for the production of predominantly ethene and/or propene, it may be advantageous to co-feed other alkenes, such as butenes, even if said process also produces said other alkenes.

Preferably, therefore, the unsaturated hydrocarbon fed to the autothermal cracker process of the present invention comprises at least one unsaturated hydrocarbon other than an alkene, such as at least one of a diene and an alkyne. More preferably, there is fed to the autothermal cracker at least one unsaturated hydrocarbon other than an alkene and less than 1wt%, such as less than 0.5wt%, of individual alkenes, such as ethene and propene, based on the weight of paraffinic hydrocarbon fed to the reactor. Even more preferably, there is fed to the autothermal cracker at least one unsaturated hydrocarbon other than an alkene and less than 1wt%, such as less than 0.5wt% of total alkenes, based on the weight of paraffinic hydrocarbon fed to the reactor. Most preferably, the feed to the autothermal cracker comprises at least one of a diene and an alkyne, and has a substantial absence of alkene.

In an alternative embodiment, the unsaturated hydrocarbon fed to the autothermal cracker process of the present invention may comprise at least one unsaturated hydrocarbon other than an aromatic compound.

The unsaturated hydrocarbon may derive from the product stream of a conventional steam cracking reactor. Alternatively the unsaturated hydrocarbon may derive from the off gas stream of a fluid catalytic cracking reactor or may derive from the off gas streams of a delayed coker unit, a visbreaker unit or an alkylation unit. In addition the unsaturated hydrocarbon may be provided by a plastics recycling process e.g. pyrolytic polymer cracking.

In one embodiment of the present invention the unsaturated hydrocarbon is provided as a portion of the product stream from a polymer cracking reactor. As well as

unsaturated hydrocarbons, the product stream from the polymer cracking reactor may also comprise paraffinic hydrocarbons and, hence, may also provide at least a portion of the paraffinic hydrocarbon fed to the process of the present invention.

5 The autothermal cracking reactor produces a product stream comprising unsaturated hydrocarbons (olefins and other unsaturated hydrocarbons). In a preferred embodiment of the invention the unsaturated hydrocarbon fed to the autothermal cracking reactor derives from the autothermal cracking product stream.

Consequently the present invention also provides a process for the production of olefins which process comprises the steps of:

- 10 (a) feeding a paraffinic hydrocarbon-containing feedstock and a molecular oxygen-containing gas to an autothermal cracker wherein they are reacted in the presence of a catalyst capable of supporting combustion beyond the normal fuel rich limit of flammability to provide a hydrocarbon product stream comprising olefins
- (b) recovering at least a portion of the olefins produced in step (a) and
- 15 (c) recycling at least one unsaturated hydrocarbon produced in step (a) back to the autothermal cracker.

In one preferred embodiment, the hydrocarbon product stream produced in step (a) is separated into a first stream comprising hydrocarbons containing less than 4 carbon atoms and a second stream comprising hydrocarbons containing at least 4 carbon

20 atoms.

Consequently a further embodiment of the invention provides a process for the production of ethene and/or propene which process comprises the steps of:

- (a) feeding a paraffinic hydrocarbon-containing feedstock and a molecular oxygen-containing gas to an autothermal cracker wherein they are reacted in the presence of a
- 25 catalyst capable of supporting combustion beyond the normal fuel rich limit of flammability to provide a hydrocarbon product stream comprising ethene and/or propene
- (b) separating the hydrocarbon product stream produced in step (a) into a first stream comprising hydrocarbons containing less than 4 carbon atoms and a second
- 30 stream comprising hydrocarbons containing at least 4 carbon atoms, including at least one unsaturated hydrocarbon containing at least 4 carbon atoms
- (c) recovering ethene and/or propene from the first stream and
- (d) recycling at least a portion of the second stream to the autothermal cracker.

In this embodiment, preferably the unsaturated hydrocarbon containing at least 4 carbon atoms is recovered from the second stream and recycled to the autothermal cracker.

5 The unsaturated hydrocarbon containing at least 4 carbon atoms may be any unsaturated compound as herein described above containing at least 4 carbon atoms. Preferably the unsaturated hydrocarbon containing at least 4 carbon atoms is selected from 1,2 butadiene, 1, 3 butadiene, 1,3 pentadiene, 1,4 pentadiene and cyclopentadiene and is advantageously 1, 3 butadiene.

10 As stated above, in a second preferred embodiment the unsaturated hydrocarbon may be an alkyne such as acetylene, propyne and/or a butyne.

Consequently, the present invention also provides a process for the production of ethene and/or propene which process comprises the steps of:

- (a) feeding a paraffinic hydrocarbon-containing feedstock and a molecular oxygen-containing gas to an autothermal cracker wherein they are reacted in the
15 presence of a catalyst capable of supporting combustion beyond the normal fuel rich limit of flammability to provide a hydrocarbon product stream comprising ethene and/or propene, and at least one alkyne
- (b) recovering at least a portion of the ethene and/or propene produced in step (a) and
- 20 (c) recycling at least a portion of the at least one alkyne produced in step (a) back to the autothermal cracker.

In this preferred embodiment, it has been found that co-feeding at least one alkyne can provide significant improvements in ethene yield and, in addition, that co-feeding alkynes can suppress methane yield.

25 A single alkyne or a mixture of alkynes may be passed to the autothermal cracker. Alternatively, a mixture of one or more alkynes with one or more other unsaturated compounds, such as one or more alkenes and/or dienes, may be passed to the autothermal cracker.

30 As stated above, at least a portion of the unsaturated hydrocarbon derives from the autothermal cracking product stream itself i.e. from the hydrocarbon product stream. If required, the unsaturated hydrocarbon derived from the hydrocarbon product stream may be supplemented by additional unsaturated hydrocarbon from one or more other sources, such as from the product stream of a conventional steam cracking reactor, the

pressure. Pressures of 1-40 barg may be suitable, preferably a pressure of 1-5 barg e.g. 1.8 barg is employed. However a total pressure of greater than 5 barg may be used, usually a total pressure of greater than 15 barg. Advantageously the autothermal cracker is operated in a pressure range of between 15-40 barg, such as between 20-30 barg e.g. 25 barg.

Where the unsaturated hydrocarbon is an alkene, an aromatic compound or a mixture of alkenes and/or aromatic compounds, the autothermal cracker is preferably operated at a total pressure of greater than 5 barg, usually a total pressure of greater than 15 barg, and advantageously in a pressure range of between 15-40 barg, such as between 20-30 barg e.g. 25 barg.

Preferably, the paraffinic hydrocarbon-containing feedstock, the gas comprising at least one unsaturated hydrocarbon and the molecular oxygen-containing gas are fed to the autothermal cracker in admixture under a Gas Hourly Space Velocity (GHSV) of greater than $80,000 \text{ hr}^{-1}$. Preferably, the GHSV exceeds $200,000 \text{ hr}^{-1}$, especially greater than $1,000,000 \text{ hr}^{-1}$. For the purposes of the present invention GHSV is defined as:- (volume of total feed at NTP / hour) / (volume of catalyst bed).

Suitably the catalyst is a supported platinum group metal. Preferably, the metal is either platinum or palladium, or a mixture thereof. Where the unsaturated hydrocarbon is an alkyne (or mixture comprising at least one alkyne), the metal preferably comprises a mixture of platinum and palladium.

Although a wide range of support materials is available, it is preferred to use alumina as the support. The support material may be in the form of spheres, other granular shapes or ceramic foams. Preferably, the foam is a monolith which is a continuous multichannel ceramic structure, frequently of a honeycomb appearance. A preferred support for the catalytically active metals is a gamma alumina. The support is loaded with platinum and/or palladium by conventional methods well known to those skilled in the art. Advantageously catalyst promoters may also be loaded onto the support. Suitable promoters include copper and tin. Usually the products are quenched as they emerge from the autothermal cracker such that the temperature is reduced to less than 650°C within less than 150 milliseconds of formation.

Where the pressure of the autothermal cracker is maintained at a pressure of between 1.5-2.0 barg usually the products are quenched and the temperature reduced to less than 650°C within 100-150 milliseconds of formation.

Where the pressure of the autothermal cracker is maintained at a pressure of between 2.0-5.0 barg usually the products are quenched and the temperature reduced to less than 650°C within 50-100 milliseconds of formation.

5 Where the pressure of the autothermal cracker is maintained at a pressure of between 5.0-10.0 barg usually the products are quenched and the temperature reduced to less than 650°C within less than 50 milliseconds of formation.

Where the pressure of the autothermal cracker is maintained at a pressure of between 10.0-20.0 barg usually the products are quenched and the temperature reduced to less than 650°C within 20 milliseconds of formation.

10 Finally where the pressure of the autothermal cracker is maintained at a pressure of greater than 20.0 barg usually the products are quenched and the temperature reduced to less than 650°C within 10 milliseconds of formation.

This avoids further reactions taking place and maintains a high olefin selectivity.

15 The products may be quenched using rapid heat exchangers of the type familiar in steam cracking technology. Additionally or alternatively, a direct quench may be employed. Suitable quenching fluids include water.

The present invention usually provides a percentage conversion of gaseous paraffinic hydrocarbon of greater than 40%, preferably greater than 50%, and most preferably greater than 60%.

20 Furthermore the present invention usually provides a selectivity towards mono-olefins of greater than 50%, preferably greater than 60%, and most preferably greater than 70%.

The invention will now be illustrated in the following examples and Figure 1.

Figure 1 represents a schematic view of an autothermal cracking apparatus.

25 Examples

Autothermal Cracking Apparatus

Figure 1 depicts an autothermal cracking apparatus comprising a quartz reactor, 1, surrounded by an electrically-heated furnace, 2. The reactor, 1, is coupled to an oxygen-containing gas supply, 3, and a hydrocarbon feed supply, 4 (for both the
30 paraffinic hydrocarbon and unsaturated hydrocarbon). The hydrocarbon feed supply, 4, is pre-heated in an electrically heated furnace, 5. Optionally, the hydrocarbon feed may comprise a further co-feed such as hydrogen and a diluent such as nitrogen. In use, the reactor, 1, is provided with a catalyst zone, 6, which is capable of supporting

combustion beyond the fuel rich limit of flammability and comprises a catalyst bed, 7. The catalyst bed, 7, is positioned between heat shields, 8, 9.

In use, the furnace, 2, is set so as to minimise heat losses. As the reactants contact the catalyst bed, 7, some of the hydrocarbon feed combusts to produce water and carbon
5 oxides. The optional hydrogen co-feed also combusts to produce water. Both of these combustion reactions are exothermic, and the heat produced therefrom is used to drive the cracking of the hydrocarbon to produce olefin.

Catalyst A

An auto-thermal cracking catalyst comprising 3wt% platinum and 1wt% copper
10 deposited on an alumina foam (15mm diameter x 30mm deep, 30 pores per inch supplied by Vesuvius Hi-Tech Ceramics, Alfred, NY USA) was prepared by repeated impregnation with solutions of tetraamineplatinum (II) chloride and copper (II) chloride in deionised water. The metal salt solutions were of sufficient concentration to achieve the desired loadings of Pt and Cu if all the metal salt were incorporated into the final
15 catalyst formulation. After each impregnation, any excess solution was removed, and the alumina foam was dried in air at 120°C-140°C and calcined in air at 450°C before the next impregnation. Once all the solution had been adsorbed, the foams were dried and reduced under hydrogen/nitrogen atmosphere at 650-700°C for 1 hour.

Catalyst B

An auto-thermal cracking catalyst comprising platinum and palladium deposited
20 on alumina spheres was prepared by impregnation, using incipient wetness, of 100g of alumina spheres (supplied by Condea, 1.8mm diam. alumina spheres, Surface Area 210 m²/g), with a solution containing 4.415g of tetraamineplatinum (II) chloride and 0.495g of tetraaminepalladium (II) chloride in deionised water. The spheres were dried at
25 120°C for 1 hour and then calcined, in air, at 1200°C for 6 hours.

Example 1

The auto-thermal cracking catalyst comprising platinum and copper deposited on alumina foam (two blocks of Catalyst A resulting in a bed 60mm deep) was placed in the autothermal cracker and the cracker was heated to 850°C.

30 A feed stream comprising ethane, nitrogen and hydrogen was passed to the autothermal cracker. Oxygen was then passed to the autothermal cracker to initiate the reaction. The hydrogen to oxygen volume ratio was maintained at 1.9:1 (v/v). The reaction was performed at atmospheric pressure.

Samples were analysed at oxygen to ethane feed ratios of 0.35, 0.44, 0.53 and 0.61 (v/v).

The nitrogen was then replaced with a feed stream comprising 9.65 volume % of 1, 3 butadiene in nitrogen and the analysis repeated.

5 The % conversion of ethane and the selectivity towards ethylene was measured and the results are shown in table 1.

Example 2

Example 1 was repeated using a hydrogen to oxygen volume ratio of 1:1 (v/v). The % conversion of ethane and the selectivity towards ethylene was measured and the
10 results are shown in table 2.

Example 3

Example 1 was repeated using a hydrogen to oxygen volume ratio of 0.5:1 (v/v). The samples were taken at oxygen to ethane feed ratios of 0.35, 0.44, and 0.53 (v/v). The % conversion of ethane and the selectivity towards ethylene was measured
15 and the results are shown in table 3.

20

25

30

Table1

Autothermal cracking of ethane and ethane with butadiene over a Pt-Cu catalyst with an hydrogen to oxygen volume ratio of 1.9:1 (v/v).

	ethane butadiene	ethane butadiene	ethane butadiene	ethane butadiene	ethane butadiene
total feed rate nl/min	9.03 9.02	9.19 9.18	9.18 9.17	9.16 9.11	
O ₂ : C ₂ H ₆ (v/v)	0.353 0.353	0.435 0.435	0.527 0.527	0.605 0.605	
H ₂ :O ₂ (v/v)	1.994 1.986	1.958 1.969	1.868 1.886	1.841 1.826	
N ₂ :O ₂ (v/v)	0.543 0.490	0.492 0.433	0.446 0.387	0.426 0.375	
1,3-butadiene : ethane (v/v)	--- 0.020	--- 0.022	--- 0.024	--- 0.027	
ethane conversion (%)	46.00 42.87	58.74 55.88	74.76 72.19	84.65 82.40	
oxygen conversion (%)	98.42 98.12	98.30 98.42	98.48 98.75	98.73 98.84	
Butadiene conversion (%)	--- 93.05	--- 96.24	--- 97.66	--- 100.00	
Ethene yield (g per 100g ethane feed)	36.50 35.59	44.93 44.87	53.16 54.13	55.87 57.93	
Aromatics yield (g per 100g ethane feed)	0.03 0.08	0.03 0.04	0.14 0.02	0.22 0.02	
Ethene selectivity (g per 100g ethane converted)	79.35 83.03	76.49 80.29	71.11 74.98	66.00 70.30	

Table 2:

Autothermal cracking of ethane and ethane with butadiene over a Pt-Cu catalyst with an hydrogen to oxygen volume ratio of 1:1 (v/v).

	ethane butadiene	ethane butadiene	ethane butadiene	ethane butadiene	ethane butadiene	ethane butadiene	ethane butadiene	
total feed rate (nl/min)	7.62	7.62	7.77	7.76	7.76	7.74	7.71	7.66
O2 : C2H6 (v/v)	0.353	0.353	0.435	0.435	0.527	0.527	0.602	0.602
H2:O2 (v/v)	0.996	0.994	1.069	1.068	1.055	1.048	1.058	1.046
N2:O2 (v/v)	0.538	0.484	0.483	0.433	0.443	0.400	0.431	0.378
1,3-butadiene : ethane (v/v)	---	0.021	---	0.023	---	0.026	---	0.028
ethane conversion (%)	47.86	46.15	60.97	59.14	77.10	75.43	86.44	84.98
oxygen conversion (%)	98.80	98.69	98.85	98.74	98.82	98.79	98.94	98.97
butadiene conversion (%)	---	92.86	---	92.01	---	97.47	---	98.37
Ethene yield (g/100g ethane feed)	35.59	36.14	44.10	44.98	52.13	53.58	54.35	56.33
Aromatics yield (g per 100g ethane feed)	0.03	0.03	0.02	0.05	0.03	0.13	0.10	0.13
Ethene selectivity (g per 100g ethane converted)	74.36	78.31	72.33	76.06	67.61	71.03	62.87	66.29

Table 3:

Autothermal cracking of ethane and ethane with butadiene over a Pt-Cu catalyst with an hydrogen to oxygen volume ratio of 0.5:1 (v/v).

	ethane	ethane	ethane	ethane	ethane	ethane
		butadiene		butadiene		butadiene
total feed rate nl/min	6.95	6.95	6.76	6.74	6.62	6.58
O ₂ : C ₂ H ₆ (v/v)	0.435	0.435	0.527	0.527	0.605	0.605
H ₂ :O ₂ (v/v)	0.546	0.542	0.474	0.477	0.460	0.441
N ₂ :O ₂ (v/v)	0.488	0.442	0.452	0.399	0.425	0.378
1,3-butadiene:ethane (v/v)	---	0.024	---	0.025	---	0.030
ethane conversion (%)	64.01	63.17	78.83	79.02	88.11	87.97
oxygen conversion (%)	98.43	98.42	98.63	98.64	98.86	98.85
butadiene conversion (%)	---	98.59	---	95.49	---	93.80
Ethene yield (g per 100g ethane feed)	43.84	45.62	50.63	51.80	51.68	53.03
Aromatics yield (g per 100g ethane feed)	0.01	0.05	0.08	0.08	0.23	0.34
Ethene selectivity (g per 100g ethane converted)	68.49	72.21	64.23	65.56	58.66	60.29

It can be seen from all the above examples that the ethene yield is generally increased and that in all cases with the addition of butadiene the ethene selectivity is increased. Furthermore it can also be seen that the addition of the butadiene does not result in any significant carbon formation on the catalyst surface due to the fact that only low amounts of aromatics are produced.

Example 4

The auto-thermal cracking catalyst comprising platinum and palladium deposited on alumina spheres (Catalyst B) was placed in the autothermal cracker and the cracker was heated to 850°C. Catalyst bed dimensions were 15mm diameter by 60mm deep

A feed stream comprising ethane, nitrogen and hydrogen was passed to the autothermal cracker. Oxygen was then passed to the autothermal cracker to initiate the

reaction. The hydrogen to oxygen volume ratio was maintained at 0.7:1 (v/v). The reaction was performed at atmospheric pressure.

Samples were analysed at three oxygen : hydrocarbon feed ratios in the range 0.51-0.60 wt/wt.

5 Acetylene was then added at a level of 2.5vol% of acetylene in ethane and the analyses repeated.

The % conversion of ethane and the selectivity towards ethylene was measured and the results are shown in table 4 for the data at O₂:hydrocarbon (ethane plus acetylene) weight ratios of ca. 0.51, 0.56 and 0.60.

10 It can be seen from Table 4 that the ethene yield and selectivity are both increased with the addition of acetylene. Furthermore it can also be seen that the addition of the acetylene does not result in any significant carbon formation on the catalyst surface due to the fact that only low amounts of aromatics are produced.

15 In addition, and surprisingly, methane yield is observed to fall on addition of acetylene. It might be expected that the methane yield would increase since methane is a secondary product of the dehydrogenation / cracking reaction of ethane to produce ethylene. Thus, the presence of acetylene appears to inhibit methane formation.

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Table 4:

Autothermal cracking of ethane and ethane with acetylene over a Pt-Pd catalyst with an hydrogen to oxygen volume ratio of 0.7:1 (v/v).

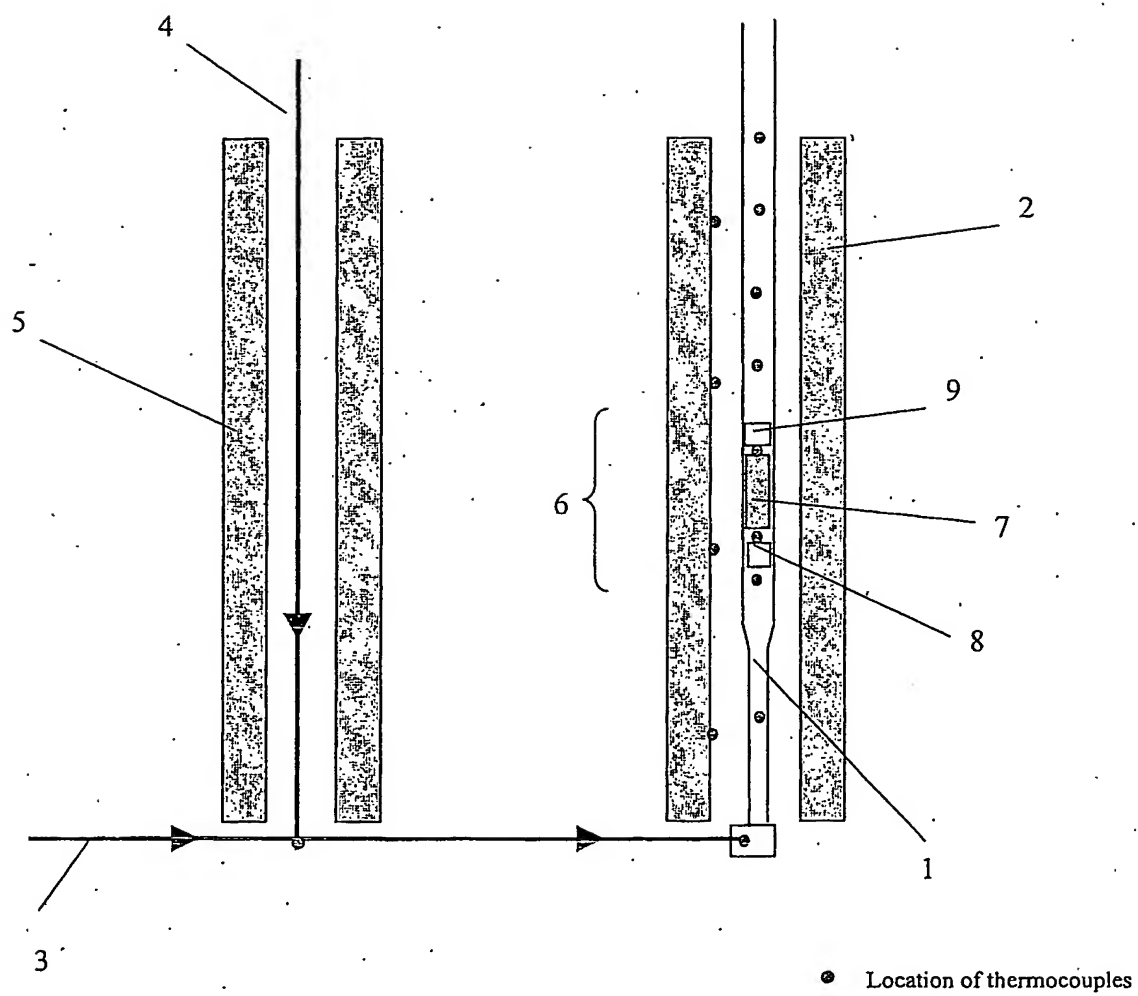
	Ethane	ethane plus acetylene	ethane	ethane plus acetylene	ethane	ethane plus acetylene
total feed nl/min	6.02	6.00	5.98	5.96	5.91	5.94
O ₂ /C ₂ H ₆ (v/v)	0.488	0.502	0.526	0.541	0.563	0.571
H ₂ :O ₂ (v/v)	0.701	0.701	0.699	0.699	0.697	0.697
N ₂ :O ₂ (v/v)	0.598	0.592	0.582	0.574	0.565	0.566
acetylene: ethane (v/v)	---	0.026	---	0.026	---	0.026
O ₂ /hydrocarbon (wt/wt)	0.520	0.524	0.561	0.565	0.600	0.595
ethane conversion (%)	67.5	73.1	73.8	78.5	79.1	82.2
oxygen conversion (%)	99.4	99.3	99.4	99.4	99.3	99.5
Ethene yield (g per 100g ethane feed)	45.17	50.41	48.13	52.62	49.77	53.68
Methane yield (g per 100g ethane feed)	4.02	3.96	4.90	4.74	5.75	5.37
Aromatics yield (g per 100g ethane feed)	0.000	0.009	0.000	0.010	0.003	0.014
Ethene selectivity (g per 100g ethane converted)	67.0	69.0	65.2	67.1	62.9	65.3

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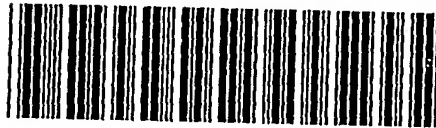
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Figure 1



PCV/GB2004/001278



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